Calcined clays for low carbon cement: Rheological behaviour in fresh Portland cement pastes

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\begin{abstract}
In this paper the rheological behavior of fresh Portland cement pastes mixed with different calcined clays was analyzed. For this purpose, two samples of Portland cement with different mineral composition (one with low C\textsubscript{3}A and high C\textsubscript{3}S content and another with low C\textsubscript{3}S and high C\textsubscript{3}A) were used combined with different replacement percentages of two calcined clays (two different metakaolin). Grounded α-quartz was used as control as well. Both mineral admixtures had different crystallinity and morphology: the α-quartz is fully crystalline while metakaolin is completely amorphous with a very small crystalline fraction giving very high pozzolanic properties in the vitreous state. All determinations were performed in the hydration latency period. The results show that the fresh Portland cement paste with low C\textsubscript{3}A(%) content and high C\textsubscript{3}S(%) present great shear strength and the replacement with calcined clays affects the rheological behavior of the fresh pastes depending on the greater or lower pozzolanic reactivity of the mineral addition.
\end{abstract}

\section*{1. Introduction}
The properties of a resulting fresh paste \cite{1–3} depend on the nature of the minerals added and the Portland cement types. Mineral additions play a lesser or greater role in cement hydration according to their nature, chemical character, morphology, particle size and addition replacement ratio along with the Portland cement type (PC), their latent period. Fluidity, for example is an important property for fresh concrete mortar or paste mixing, casting, placement and consolidation. Fluidity may be assessed with rheometric trials to determine, for instance, shear stress or stress (τ) by varying the rotational speed. The resulting flow curves provide a measure of fluidity \cite{4,5}. In this study, the parameters defined to analyse the effect of pozzolanic or non-pozzolanic mineral additions on the apparent viscosity of each fresh paste during cement hydration latency were as follow: the type of cycle to be applied, on the grounds of the largest possible area of hysteresis characteristic of paste thixotropy \cite{6}, the responses obtained in Portland cements with different potential mineralogy \cite{4} and their rheological behaviour in the presence of the crystalline silica α-quartz filler and two calcined clays with aluminic chemical character, according to Talero \cite{7}.

\section*{2. Materials and methods}
Two Portland cements (PC) with widely different potential mineralogical compositions were chosen to ensure that the results would be extensive to any type of PC. The first one, denominated PC1 and characterized by its high C\textsubscript{3}A(%) content, whose mineralogical composition was found to be followed: 51.0% C\textsubscript{3}S, 16.5% C\textsubscript{2}S, 14.0% C\textsubscript{3}A and 5.5% C4AF, a density of 3.08, a Blaine specific surface, BSS, of 319 m\textsuperscript{2}/kg and Na\textsubscript{2}Oeq of 1.24% (>0.6%). On the other hand, the second Portland cement, PC2, was selected due to its low C\textsubscript{3}A(%) and high C\textsubscript{3}S(%) contents; its detail mineralogical composition was: 79.5% C\textsubscript{3}S, 2.5% C\textsubscript{2}S, R±0.0% C\textsubscript{3}A(<1.0%) and 10.0% C4AF, a density of 3.21, a BSS of 329 m\textsuperscript{2}/kg and Na\textsubscript{2}Oeq of 0.56% (<0.6%). Three mineral additions were chosen as follows:

- a quartz one, Q, with a SiO\textsubscript{2} content of over 99%, a density of 2.70, a BSS of 395 m\textsuperscript{2}/kg and a loss on ignition of 0%, being therefore additionally, siliceous in nature and acid in chemical character;
• a nearly pure metakaolin M (95.0%), with a 48% reactive silica content [8] and a 29% reactive alumina content [9], being its density 2.52 and its BSS, 333 m²/kg, and
• a metakaolin blended with quartz, MQ (50 mass%) having a 38% reactive silica content [8] and a 15% reactive alumina content [9], being its density 2.55, and its BSS, 398 m²/kg.

The metakaolins were prepared by calcining kaolin, with and without 50% quartz, at 750 °C. The replacement ratios used were 20% and 40% for every mineral addition M, MQ and Q, all by Portland cement mass.

The Frattini test was used to analyze the blended cements mentioned [10]. The calcium hydroxide content in the aqueous solution, in contact with the hydrated sample, was kept at 40 °C during the first hydration stage and then compared to the calcium hydroxide isothermal solubility in an alkaline solution kept at the same temperature. Data was taken after 60 min and after a day besides the findings for the first nadir calorimetric conduction, Initial Setting Time (I.S.T.), Final Setting Time (F.S.T.) Table 1.

Rheological trials were also run on a rotational rheometer fitted with a profiled rotor blade with serrated surface [Internal Diameter (RI) = 19.010 mm; height (h) = 55 mm], a profiled cylinder, a temperature control unit for coaxial cylinders and a circulation thermostat. A scheme was made to show the evolution of the cement pastes as they reach the biggest hysteresis loop (thixotropic behavior). A continuous variation of shear rate was applied assuming that at the maximum rate the structure would be close to be destroyed and at the minimum it would not rebuild [11]. A control shear rate test (or CR test) was chosen for every case. The scheme designed (Fig. 1) was as follows: 10° from 0 to 45 rad/s [A0 point]; 10° from 0 to 9 rad/s [C0 point]; 10° from 9 to 0 rad/s [C1 point]; 10° rest [C2 point]; 10° from 0 to 9 rad/s; 10° from 9 to 27 rad/s; 10° at 27 rad/s; 10° from 27 to 45 rad/s [A0 point]; 30° at 45 rad/s [B2 point]; and 10° from 45 to 0 rad/s [C3 point]. Trials were conducted during latent hydration period at 25 °C because the viscosity of these materials is strongly dependent on the shear rate applied and on the degree of hydration of the cement paste, so this experimental scheme minimizes the different cement hydration rate influence [11–13]. Yield stress (\( \tau_0 \)) parameter values were also adjusted with the model that provides a better regression, in this case was Casson equation (Eq. (1)) [11–13]. Yield stress (\( \tau_0 \)) parameter values were also adjusted with the model they provides a better regression, in this case was Casson equation (Eq. (1)) [0-0].

\[
\tau = \left( \tau_0 + (\eta_p \cdot \dot{\gamma})^{1/3} \right)^2
\]

For the rheometric trials, the samples were hydrated at a water:binder (cement + filler) ratio (w/b) of 0.5 in every case. The fresh pastes were mixed manually for 2 min in a porcelain capsule, were stored in a water bath at 25 °C until they were tested and poured into the viscometer annulus. Test times were made to concur during the hydration latency period. The latency period was determined with prior calorimetric trials [23,14]. X-ray diffraction was applied to identify the hydrated and unhydrated compounds present in the resulting pastes, likewise during hydration latency.

### 3. Results and discussion

Table 1 show determined [CaO] and [OH\(^{-}\)]. Note that the PC/M 60/40 pastes showed pozzolanic activity at the first age, in the case of PC1, but in the case of PC2, this phenomenon was seen later. These PC1/M mixes showed a higher pozzolanicity at that stage because the rate of the hydration reaction was been countered or compensated for by the fixation of the calcium hydroxide resulting from the high, fast and early pozzolanic reaction of M.

On the other hand, the calcined clay MQ naturally, showed lower pozzolanic activity than the calcined clay M at the same stage. So 50% of quartz content present in MQ, naturally, exhibited no pozzolanic activity with neither of the two Portland cements.

### Table 1

<table>
<thead>
<tr>
<th>Blended cements</th>
<th>Age</th>
<th>[CaO] mM(^{-1})</th>
<th>[OH(^{-})] mM(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 min</td>
<td>60 min</td>
<td>1 h Min.</td>
</tr>
<tr>
<td>PC1</td>
<td>39.50</td>
<td>40.00</td>
<td>34.65</td>
</tr>
<tr>
<td>PC1/M 80/20</td>
<td>36.50</td>
<td>29.50</td>
<td>35.50</td>
</tr>
<tr>
<td>PC1/M 50/40</td>
<td>26.60</td>
<td>26.75</td>
<td>26.70</td>
</tr>
<tr>
<td>PC1/MQ 80/20</td>
<td>35.10</td>
<td>30.75</td>
<td>37.30</td>
</tr>
<tr>
<td>PC1/MQ 60/40</td>
<td><strong>32.80</strong></td>
<td><strong>24.25</strong></td>
<td><strong>35.10</strong></td>
</tr>
<tr>
<td>PC1/Q 60/40</td>
<td>35.45</td>
<td>33.00</td>
<td>33.85</td>
</tr>
<tr>
<td>PC1/Q 80/20</td>
<td>31.75</td>
<td>23.00</td>
<td>30.10</td>
</tr>
<tr>
<td>PY6</td>
<td>49.15</td>
<td>24.50</td>
<td>43.35</td>
</tr>
<tr>
<td>PC2/M 60/40</td>
<td>46.70</td>
<td>30.75</td>
<td>45.55</td>
</tr>
<tr>
<td>PC2/M 80/20</td>
<td>42.20</td>
<td>35.00</td>
<td>42.10</td>
</tr>
<tr>
<td>PC2/Q 50/20</td>
<td>49.30</td>
<td>35.00</td>
<td>41.00</td>
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<tr>
<td>PC2/Q 60/40</td>
<td>44.20</td>
<td>32.00</td>
<td>42.10</td>
</tr>
<tr>
<td>PC2/Q 70/40</td>
<td>46.00</td>
<td>34.50</td>
<td>44.70</td>
</tr>
<tr>
<td>PC2/Q 80/40</td>
<td><strong>43.50</strong></td>
<td><strong>43.50</strong></td>
<td><strong>42.90</strong></td>
</tr>
</tbody>
</table>

In bold, blended cements that fulfilled the Frattini test.
Initially, this higher rate of reaction in the PC fraction is due, among other possible reasons, to water (from the mixing water) adsorption on the surface of the particles of the pozzolanic additions, a process that may be termed direct [2,13] and non-direct [2,13] hydration stimulation, which differs from “indirect” stimulation [7,14].

Furthermore, the rate of calcium hydroxide (CH) generation and evolution was very low in M and MQ containing cement pastes during the first 24 h, which is consistent with the high pozzolanic activity exhibited by these two pozzolans (Table 1).

Nonetheless, the amount of CH generated was observed to increase more in both PC when blended with MQ. It was due more to the direct stimulation of its 50% Q (providing further evidence that this crystalline mineral stimulates hydration reactions directly [2,13]) than to the lesser Al₂O₃ content of MQ (0.5Al₂O₃ content of M).

When Q filler partially replaced PC1 in the respective blends, [OH⁻] in the liquid phase of the resulting pastes it declined as the replacement ratio rose. That finding attested to the physical dilution effect and hence of the Na₂Oeq content in PC1 and the portlandite generated after initial hydration. In contrast, when PC2 was partially replaced by Q filler (Table 1), medium basicity rose in the early hydration reactions, a development that was intensified by rising replacement ratios. At longer test stages, however, the liquid phase in all the blended cements was less alkaline than the respective pure Portland cement. That finding inferred that Q stimulated Portland cement hydration is more effectively when the C₃A content was high than when C₃S was high. Therefore, of the two PC phases, C₃A are more logically prone to greater and faster hydration stimulation.

Fig. 2 plot the shear stress against the shear applied (CR test) to the fresh pastes made with PCs and their blends with M, MQ and Q. The singular points shown in Fig. 1 were identified for all the rheological tests. The fresh paste values for the PCs and their family of blended cements are given in Table 2.

3.1. Rheological behavior with Q filler

When Q filler was added to PC1, shear strength rose at most of the singular points and where that was the case, the effect intensified when the replacement ratio was raised to 40%. That increase in the apparent viscosity of the fresh paste induced by the inclusion of a crystalline mineral.
of Q filler was due to the larger number of Q particles present in the paste (which, as wholly crystalline, were neither pozzolanic nor hydraulic). Their presence stimulated hydration of the fraction of PC1 directly [0,0] and non-directly [0,0] and with it the formation of the respective hydration products sourced primarily from C3A, namely slow-forming ettringite, ett-rf [0,0] and AFm (Fig. 3). These latter prompted a decline in fresh paste fluidity. The greater amount of the hydration products that could form would be proportional to the amount of hydration water available to the PC1 in the blend with Q filler (in this case, PC1/Q 60/40).

Furthermore, in fresh paste, these stimulating effects could be curbed at some ages as a result of the physical dilution of PC1 by Q filler. In fact, a chemical dilution was produced in liquid phase of the paste, and therefore its major constituents, portlandite and especially Na2Oeq. These phases were generated during initial PC1 hydration (for in such circumstances, paradoxically, the amounts of ett-rf and AFm formed by the 60% PC1 in the blend should potentially be greater than the amounts of pure PC1: see Fig. 3). The inescapable result would be greater fresh paste viscosity.

The foregoing is reinforced by the opposite rheological behaviour observed in families PC1/Q and PC2/Q at the same singular points. Viscosity was higher in the PC1/Q family fresh paste when the blend contained 40% filler (see Table 2). Conversely, in PC2/Q, viscosity was observed to be higher with a 20% replacement ratio.

### Table 2

<table>
<thead>
<tr>
<th>Cement</th>
<th>pH</th>
<th>w/c ratio</th>
<th>Age (min.)</th>
<th>τ0 (Pa)</th>
<th>A1</th>
<th>B1</th>
<th>C1</th>
<th>C2</th>
<th>A2</th>
<th>B2</th>
<th>C1</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1/MQ 60/40</td>
<td>12.27</td>
<td>0.65</td>
<td>105</td>
<td>225.36</td>
<td>367.60</td>
<td>227.20</td>
<td>34.34</td>
<td>112.50</td>
<td>130.20</td>
<td>125.30</td>
<td>126.50</td>
</tr>
<tr>
<td>PC1/M 60/40</td>
<td>12.25</td>
<td>0.50</td>
<td>95</td>
<td>220.52</td>
<td>282.10</td>
<td>122.70</td>
<td>34.32</td>
<td>105.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>PC1/Q 60/40</td>
<td>12.29</td>
<td>0.50</td>
<td>100</td>
<td>74.26</td>
<td>95.73</td>
<td>146.60</td>
<td>36.73</td>
<td>56.98</td>
<td>56.98</td>
<td>56.98</td>
<td>56.98</td>
</tr>
<tr>
<td>PC2/MQ 60/40</td>
<td>12.17</td>
<td>0.50</td>
<td>100</td>
<td>220.52</td>
<td>225.36</td>
<td>122.70</td>
<td>34.32</td>
<td>105.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>PC2/M 60/40</td>
<td>12.25</td>
<td>0.50</td>
<td>100</td>
<td>40.32</td>
<td>161.54</td>
<td>160.00</td>
<td>48.06</td>
<td>126.20</td>
<td>126.20</td>
<td>126.20</td>
<td>126.20</td>
</tr>
<tr>
<td>PC2/Q 60/40</td>
<td>12.35</td>
<td>0.50</td>
<td>100</td>
<td>164.27</td>
<td>267.30</td>
<td>112.50</td>
<td>34.32</td>
<td>105.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>PC2/Q 80/20</td>
<td>12.37</td>
<td>0.50</td>
<td>180</td>
<td>92.84</td>
<td>92.84</td>
<td>92.84</td>
<td>34.32</td>
<td>92.84</td>
<td>92.84</td>
<td>92.84</td>
<td>92.84</td>
</tr>
</tbody>
</table>

1° Liquid phase during latent period as per the Frattini test [15,16] at 25 °C.
2° Water-cement ratio.
3° Duration of latent period as per conduction calorimetry.

#### 3.2. Rheological behavior with M and MQ calcined clays

When PC1 was replaced by the MQ and M additions, the shear stress was high in all the singular points and it also increased when the replacement level increased. This behavior can be attributed primarily to the early, rapid and very high pozzolanicity developed by the Al2O3 present in M and MQ. This stimulation phenomenon is more specific than generic, prompting more intense C3A hydration; that is, C3A hydration was more stimulated than C3S hydration. This type of stimulation of hydration reactions are termed “indirect” [3]. Furthermore, such stimulation must have been favored by the greater amount of water available: see the higher w/b ratios in Table 2.

These findings denote dilution of the silicate phase due to replacement of the PC1 by the respective metakaolin, and simultaneously, the Synergistic Effect, SE, produced between the C3A from the PC1 and the Al2O3 from the metakaolin. This phenomenon can be demonstrated by the XRD analysis (Fig. 3) that shows the presence of AFt, AFm phases and the absence of portlandite. From the rheological test, a notable recovery of shear strength occurred when the rotor stopped (C1 and C2) reaching to a shear stress two times greater than that obtained for the fresh PC1 paste.

When CP2 is replaced by M or MQ additions, the shear stress was high in all the singular points and it also increased when the percentage of replacement increases, as occurred for PC1 (somewhat...
higher than for the same points in PC1). This increase is more important when the rotor is stopped (C₁, C₂ and C₃), even exceeding the values at the same point obtained for paste with PC1, despite its high C₃A content.

These findings further support the very high reactivity of both calcined clays, M and MQ, and the intensity of the hydration stimulation induced in PC2, particularly indirectly [3]. The rise in shear stress with calcined clays replacement ratio might have been due to the same pozzolanicity as described for PC1, except that the lower AF content in PC2, which in this case must have been stimulated as a result of the formation of AFm primarily from C₄AF origin (see the respective diffractogram in Fig. 3), may have been the reason why shear stress rose somewhat less. Furthermore, while portlandite did not appear because it was consumed in the pozzolanic reaction, the intensity of the Cₛ diffraction line was observed to decline as a result of CSH gel formation, which contributes to mechanical strength, as verified by the shear stress findings (Table 2). The inference drawn from the foregoing is that, in the early stage rheological behavior tests on these fresh pastes, the very high pozzolanicity of calcined clays was specific, as noted earlier, because in the initial stages stimulation was “indirect”, inducing greater and speedier hydration in the C₃A and in the OPC. While the C₃A content in a PC is nil, as in the PC2 studied here, C₄AF hydration is likewise stimulated mostly indirectly.

4. Conclusions

1. The viscosity of any Portland cement fresh paste and their yield stress depends on the qualitative and quantitative mineralogical and chemical composition, that is, Na₂Oeq.% content especially of the cement, i.e., the alkaline element content in the liquid phase of their fresh paste, and on the amount and types of hydrated compounds generated during the hydration latency period, when the fresh paste is fluid.

2. Very early stage hydration in both Portland cements studied was stimulated directly and non-directly by the presence of mineral Q filler. Stimulation was intensified with the percentage of Portland cement replaced by Q filler, without impairing the effect associated with the physical dilution of the Portland cement and the liquid phase in its fresh paste, which prevails when stimulation weakens.

3. The two calcined clays M and MQ (aluminic pozzolans in chemical character and with very high pozzolanicity) stimulated the hydration of AF phase for both Portland cements (directly and non-directly, but especially “indirectly”) given their high \(Al_2O_3\) content and as a consequence, due to their high, speedy and early pozzolanic activity. That also induced the AFm phase formation even in the Portland cement with no C₃A(%) content, i.e., PC2. Therefore reacting with its setting regulator content in its C₄AF phase. This phenomenon proves that its outstanding pozzolanic reactivity is actually more specific than generic, inducing always more intense and speedier C₃A hydration in any Portland cement.

References